

A kinetic reaction model for biomass pyrolysis processes in Aspen Plus

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Abstract

This paper presents a novel kinetic reaction model for biomass pyrolysis processes. The model is based on the three main building blocks of lignocellulosic biomass, cellulose, hemicellulose and lignin and can be readily implemented in Aspen Plus and easily adapted to other process simulation software packages. It uses a set of 149 individual reactions that represent the volatilization, decomposition and recombination processes of biomass pyrolysis. A linear regression algorithm accounts for the secondary pyrolysis reactions, thus allowing the calculation of slow and intermediate pyrolysis reactions. The bio-oil is modelled with a high level of detail, using up to 33 model compounds, which allows for a comprehensive estimation of the properties of the bio-oil and the prediction of further upgrading reactions. After showing good agreement with existing literature data, our own pyrolysis experiments are reported for validating the reaction model. A beech wood feedstock is subjected to pyrolysis under well-defined conditions at different temperatures and the product yields and compositions are determined. Reproducing the experimental pyrolysis runs with the simulation model, a high coincidence is found for the obtained fraction yields (bio-oil, char and gas), for the water content and for the elemental composition of the pyrolysis products. The kinetic reaction model is found to be suited for predicting pyrolysis yields and product composition for any lignocellulosic biomass feedstock under typical pyrolysis conditions without the need for experimental data.

Keywords:

Aspen Plus, bio-oil, lignocellulosic biomass, process simulation, pyrolysis, reaction kinetics

* The development of the kinetic reaction model and its bibliographic validation was carried entirely out at IMDEA Energy Institute, while the experimental validation was done at EBRI.

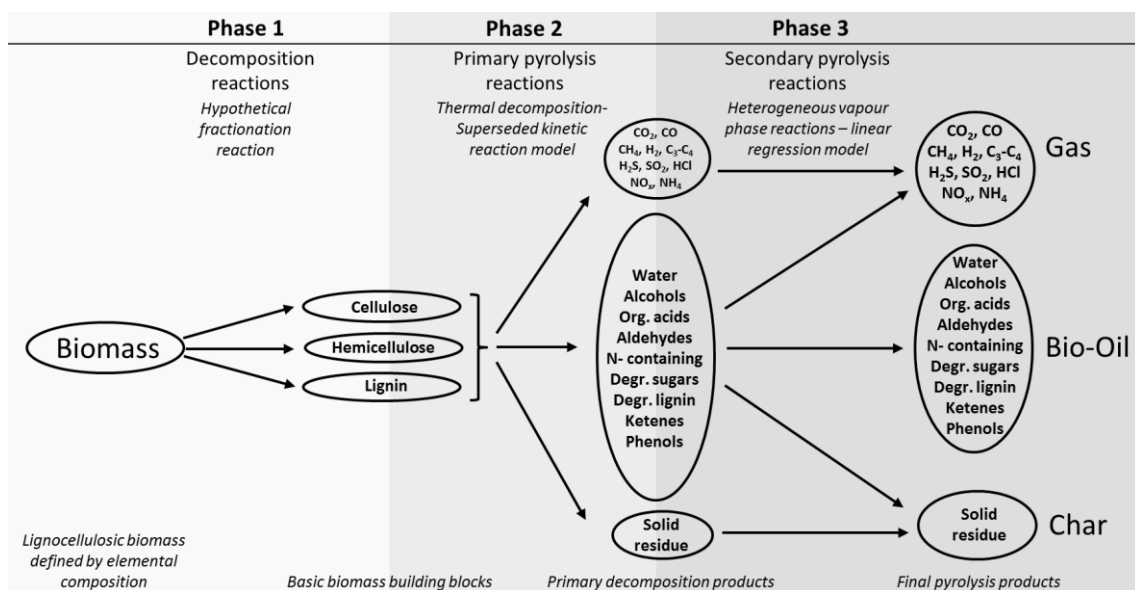
36 An efficient deployment of the existing bioenergy potential is vital for reaching the renewable
37 energy targets set up by the European Union [1]. However, biomass is a decentrally available
38 energy source of relatively low density. This increases expenses for handling and transport and
39 thereby limits the potential for industrial applications. One possibility to overcome this problem
40 is the use of fast pyrolysis for converting the biomass into bio-oil and / or char. Pyrolysis is the
41 thermal decomposition under non-oxidative atmosphere and at moderate temperatures,
42 normally around 500 °C. With lignocellulosic biomass as feedstock, it yields gases, a
43 carbonaceous residue (char) and a liquid fraction (bio-oil). The bio-oil has a similar heating value
44 as the original biomass, but a higher density and, as a liquid, it is easier to handle [2]. By varying
45 the reaction conditions, the yield of the fractions can be controlled: Fast pyrolysis maximizes the
46 liquid yield at temperatures around 500 °C and very short residence times, while slow pyrolysis
47 achieves high char yields at slightly lower temperatures around 450 °C and very long vapour
48 residence times [3]. Biomass pyrolysis is mainly in the research stage and almost no commercial
49 pyrolysis installations exist to-date [4,5]. Due to the lack of actual plant data, system analysis of
50 pyrolysis processes is normally based on process simulation. Since bio-oil is a complex substance
51 composed of hundreds of individual compounds [3,6], its modelling in process simulations is a
52 difficult task and requires major simplifications. Existing technical and environmental
53 assessments use approximations applying few model compounds, significantly simplifying the
54 bio-oil characteristics. Furthermore, they use to implement simple top-down approaches which
55 adjust the pyrolysis products of the reactor to existing literature data for a specific feedstock [7–
56 14]. This creates a dependency on experimental data and makes it difficult to simulate processes
57 with feedstock for which no experimental data is available. To avoid this drawback, a flexible
58 and predictive simulation capable of dealing with a wide range of different lignocellulosic
59 feedstock is of considerable interest. Kinetic reaction models based on thermodynamic
60 equilibrium calculations can provide this flexibility and have been developed for combustion or
61 gasification reactions [15–17], but proven to be unsuitable for predicting pyrolysis reactions
62 [18]. Current approaches for modelling pyrolysis processes focus strongly on computational fluid
63 dynamic (CFD)[19–21] or single particle models [22,23], while others consider isolated biomass
64 components (like e.g. lignin) [24] or determine only the lumped yields of the principal pyrolysis
65 products (gas, char, oil) [25–30], while they do not model their detailed composition.
66 Nevertheless, the latter is of high importance for system analysis, since emissions and other
67 environmental impacts of the process are determined to a major share by the composition of
68 the products i.e., their content of nitrogen, chlorine, sulphur etc. Knowing the detailed
69 composition of the bio-oil is also relevant for modelling downstream processes like the refining
70 / upgrading of the bio-oil to transportation fuel. Still, no work has yet been published that allows
71 a predictive calculation of the composition of pyrolysis products for varying feedstocks [31]. This
72 paper presents a kinetic reaction model able to calculate yields and composition of the pyrolysis
73 products of unknown lignocellulosic feedstock based on its biochemical composition and with a
74 minimum of input. The model can be readily implemented in Aspen Plus. In this way,
75 independency from experimental data is achieved and a valuable tool for system analysis of
76 pyrolysis processes for lignocellulosic biomass is provided. It can be used for assessing fast and
77 slow pyrolysis processes on plant and component level, and permits predicting also the influence
78 of different reactor conditions on the pyrolysis product properties [32–35]. Cross-checking the

79 results obtained from the reaction model with data obtained from specific pyrolysis experiment
 80 further allows for its validation.

81

82 2. Reaction model

83 The kinetic reaction scheme presented in this work follows the model approach of DiBlasi et al.
 84 [36], assuming an interlinked linear reaction process for the three basic biomass building blocks
 85 (cellulose, hemicellulose and lignin) [37,31]. It takes into account the primary pyrolysis reactions
 86 as well as the secondary cracking reactions. For this purpose, the pyrolysis mechanism is divided
 87 in three phases, one decomposition phase and two pyrolysis phases. Figure 1 schematically
 88 depicts the reaction mechanism implemented.



89

90 **Figure 1.** Three stage reaction scheme for pyrolysis reactions as implemented in the simulation

91 The **first phase** is a virtual reaction step that decomposes the biomass into its three principal
 92 biochemical building blocks, cellulose, hemicellulose and lignin. The **second phase** represents
 93 the decomposition and volatilization of the biomass fragments, giving a high liquid yield. This is
 94 the dominating reaction mechanism for fast pyrolysis processes with short vapour residence
 95 times. The **third phase** contains the secondary cracking and charring reactions which increase
 96 gas and char yields at the expense of liquid yield, due to secondary (catalytic) cracking reactions.
 97 These gain importance with increasing residence times and are therefore especially relevant for
 98 slow and intermediate pyrolysis reactions.

99 From the kinetic reaction modelling, the model is able to calculate the yields of key pyrolysis
 100 products for a temperature range between 420 to 650 °C and for hot vapour residence times of
 101 up to 2500 s, allowing the simulation of fast and slow pyrolysis processes for any lignocellulosic
 102 feedstock with known composition [38]. The bio-oil produced is modelled at a high level of
 103 detail, with 33 components including organic acids, aldehydes, alcohols, ketones, phenols, sugar
 104 derivatives and degraded lignin, and the char produced is modelled with a realistic elemental

105 composition. The input required by the model for calculating the pyrolysis products is listed in
106 Table 1, while the reactor model is described more in detail in the following.

107

108 **Table 1.** Biomass composition parameters as required by the reaction model.

BIOMASS COMPOSITION		
ULTIMATE ANALYSIS % wt (db)	PROXIMATE ANALYSIS % wt (ar)	Biochemical composition % wt (db)
ASH	Fixed carbon	Cellulose
CARBON	Volatile matter	Hemicellulose
HYDROGEN	Ash	Lignin
NITROGEN	Water	
CHLORINE		
SULFUR		
OXYGEN		
Alkali metal content		

109

110

111 2.1. Decomposition reactions

112 In the first stage, the biomass feedstock is decomposed into its principal building blocks
113 (cellulose, lignin and hemicellulose). This reaction step does not represent any part of the actual
114 pyrolysis reaction mechanism, but is necessary for the following interlinked reaction model. This
115 is based on the three principal building blocks of the biomass and therefore requires these
116 fractions as inputs. Hemicellulose and cellulose are represented in the simulation by its
117 monomers, C₅H₈O₄ (Xylan) and C₆H₁₀O₅ (Xylose- like cellulose monomer), respectively. While
118 cellulose and hemicellulose are compounds with relatively fixed monomer structure, lignin is
119 more heterogeneous and can give a wide range of different monomers when decomposing.
120 Lignin is therefore represented by seven different monomers with different O/C and H/C- ratios.
121 The detailed description of these monomers and their molecular structure can be found in the
122 online supplementary information (SI). Using different lignin monomers permits adjusting the
123 elemental composition of the decomposition products to the elemental composition of the
124 biomass by varying the amounts of the different lignin components [39]. The amount of each of
125 the seven lignin monomers released hence depends on the initial biomass composition. The
126 decomposition reaction is implemented in Aspen Plus in an RYield-type reactor. The yields are
127 calculated iteratively by an embedded Excel worksheet which determines the lignin composition
128 of the biomass according to its elemental composition. More details about the calculation
129 algorithm are provided, together with the properties and molecular structures of the
130 compounds, in the SI. The nitrogen content of the biomass is taken into account by including
131 two representative N containing species in the decomposition products, glutamic acid and
132 pyrrole, again with different O/C and H/C ratios to adapt to different biomass compositions.
133 Both are frequent in biomass, the amino acid represents proteins while pyrrole is the basic
134 compound of more complex, biomass typical molecules like chlorophyll or porphyrins [40–42].

135

2.2. Primary pyrolysis reactions

136 In the second phase, a kinetic reaction model is implemented for the primary pyrolysis reactions.
137 It is an interlinked model of individual decomposition reactions of cellulose, hemicellulose and
138 lignins, according to Miller & Bellan [43] and Di Blasi [36]. A good review of kinetic model
139 schemes for pyrolysis reactions is given by C. Gómez Díaz in her thesis [44]. The reaction
140 mechanism is based on several works published on the kinetics of pyrolysis reactions [39,45–
141 49]. It implements 149 individual reactions, including primary decomposition, secondary
142 decomposition, radical substitution, recombination and char volatilization reactions. The reactor
143 type can be chosen according to the pyrolysis reactor that wants to be modelled. For fast
144 pyrolysis, the RCStir reactor is used, while the RBatch- type reactor is more suitable for slow
145 pyrolysis modelling. For modelling different reactor types, the operation temperature, bed and
146 vapour residence times for the simulated reactor are required as key parameters determining
147 the reactor conditions.

148 The kinetic reaction schemes are implemented as Power Law type kinetic expressions with the
149 reaction rate calculated in AspenPlus by Equation (1).

$$150 \quad r = k * T^n * e^{-E/RT} \quad \text{Equation (1)}$$

151 With r being the rate of reaction, k the pre-exponential factor, T the absolute temperature, E
152 the activation energy and R the gas law constant.

153
154 The complete set of kinetic reactions implemented in the reactor model is given in the
155 supplementary information (SI). All compounds used are listed with their formulae and, if
156 required, their elemental structure which can also be found in the SI.

157

158 **2.3. Secondary pyrolysis reactions**

159 Secondary vapour phase reactions are complex, including partially catalytic polymerization and
160 recombination reactions for which the kinetics are largely unknown [44,50]. Nevertheless, they
161 are important and responsible for decreasing oil yields at longer hot vapour residence times.
162 The kinetic reaction mechanism does not include them and therefore tends to give too high oil
163 and too low char yields under slow pyrolysis conditions. To account for them without knowing
164 the underlying kinetic reaction mechanisms, a linear regression model based on experimental
165 results is implemented for this purpose [44,51–53]. Increased gas and char yield due to
166 heterogeneous secondary reactions depend mainly on ash alkali metal content, temperature
167 and vapour residence time [51–53]. The alkali metals contained in the ashes are of special
168 importance since they act like a catalyst for these reactions [54,55]. Based on the experimental
169 findings from literature, a polynomial approximation is implemented that corrects the fractional
170 yields accordingly. In this way, the secondary vapour reactions at longer residence times are
171 accounted for and realistic yields for slow pyrolysis reactors can be obtained.

172 All the secondary reactions are implemented in Aspen Plus as an embedded Excel sheet which
173 determines the yields of the RYield type secondary reactions reactor. The complete
174 methodology and the corresponding equations can be found in the SI.

175 **3. Verification with literature data**

176 In order to validate the reaction model as a predictive tool, it is first tested and cross-checked
 177 against data published in literature. In a previous publication, yield curves for different residence
 178 times and reaction temperatures for pine wood and wheat straw have been presented [34].
 179 These show the typical shape for biomass pyrolysis, and also the dependency of the yields on
 180 the feedstock is represented properly; with pine wood showing a significantly higher liquid yield
 181 than wheat straw and a less pronounced response to hot vapour residence time.
 182 Apart from generic and typical yield curves, only a few publications are available for in depth
 183 verification of the reaction model. The reaction model requires a set of biomass property
 184 parameters (above all elemental and biochemical composition), which are usually not given
 185 completely in publications on pyrolysis experiments. If, on the other hand, part of the required
 186 information (e.g. the biochemical biomass composition) is taken from other works or a common
 187 database like Phyllis [56], the significance of the validation is considerably reduced, since the
 188 composition of biomass of even the same type can vary substantially. Nevertheless, a few
 189 publications are available that include details of the underlying experiments for the simulation.
 190 The results are given in Table 2 (fast pyrolysis), and Table 3 (slow pyrolysis). The experimental
 191 findings from the available literature are reproduced with good agreement; only the water
 192 content of the bio-oil shows some deviation. Also the slow pyrolysis yields correspond well.
 193 Straw as a feedstock is included in Table 2 for comparison purpose, although no publication is
 194 available that provides all parameters. The influence of the biomass composition on the yields
 195 can be clearly observed, with straw as a feedstock showing lower oil and higher char yields.

196 **Table 2.** Fraction yields (fast pyrolysis, 500 °C) in comparison with literature data.

	Pine wood		Eucalyptus		Hybrid Poplar		Wheat straw	
	Sim	Lit ^(a)	Sim	Lit ^(a)	Sim	Lit ^(b)	Sim	Lit ^(c)
Gas	10.6%	10.9%	12.8%	--	12.1%	13.1%	13.8%	--
Oil	75.4%	78.3%	69.9%	70.8%	70.9%	69.7%	66.8%	--
Char	14.0%	10.9%	17.3%	--	17.0%	16.2%	19.4%	--
Oil water content	18.4%	23.8%	20.7%	16.0%	16.2%	15.8%	18.3%	--

197 (a): Oasmaa et al. [57]; (b): Ringer et al. [12]; (c): no data available

198 **Table 3.** Fraction yields (slow pyrolysis, 425 °C) in comparison with literature data.

	Pine wood	
	Sim	Lit ^(*)
Gas	27.0%	27.2%
Oil	50.1%	49.6%
Char	22.9%	23.0%

199 (*): Williams & Besler [58]

200 Another important aspect of the reaction model is the detailed modeling of the bio-oil
 201 composition. Since the analysis of the composition of bio-oil in general is difficult, very little
 202 literature is available that provides an analysis of the fractional composition of the bio-oil in
 203 combination with all biomass property parameters required for the reaction model. Table 4
 204 shows the comparison of the fractional composition of the bio-oil from two different feedstocks
 205 from literature and obtained from simulation. Again, a good agreement can be observed, with
 206 the simulation showing a tendency to give higher aldehyde contents and lower water yields. On

207 the other hand, the analysis from the literature source does not list ketones and organic acids,
 208 which are important constituents of bio-oils.

209
 210

211 **Table 4.** Fractional composition of the bio-oil in comparison with literature data [57].

	Pine Wood		Eucalyptus	
	Sim	Lit	Sim	Lit
Water	18.39%	23.8%	20.67%	25%
Acids	4.17%	--	6.69%	--
Aldehydes	22.34%	21.4%	18.94%	25%
Ketones	5.03%	-- (*)	3.68%	-- (*)
Degraded sugars	29.20%	33.3%	31.01%	30%
Others (extract.)	3.12%	3.6%	5.05%	2%
Degraded lignin	17.76%	17.9%	13.96%	17%

212 (*): Ketones not listed explicitly, but included in aldehyde fraction

213

214 **4. Experimental verification**

215 As mentioned, literature for verification is scarce, since a set of input variables is required that
 216 is often not given completely. If, on the other hand, one or more of the parameters (e.g. the
 217 biochemical composition) is taken from another source, the value of the validation is limited.
 218 Hence, our own pyrolysis experiments are used for further verifying the model.

219

220 **4.1. Experimental setup**

221 Pyrolysis experiments were conducted in a 1kg·h⁻¹ fast pyrolysis unit, using beech wood as
 222 feedstock. In order to validate the temperature response of the simulation model, several runs
 223 were conducted at different temperatures (450 °C, 500 °C, 550 °C).

224 The biomass samples were dried and ground to the particle size required for the pyrolysis
 225 reactor. The moisture and ash contents of the biomass samples were determined and their
 226 elemental composition analysed. For determining the biochemical compositions, an acid
 227 hydrolysis procedure was used. The results of the biomass analysis are given in Tables 5 and 6.

228

229 **Table 5.** Elemental composition of the beech wood feedstock (%).

C	H	N	Cl	S	O	Ash	Alk*
48.45	6.12	0.15	0	0.02	45.08	0.19	0.12

230 * Alk = Alkali metal content; double counted, already contained in ash

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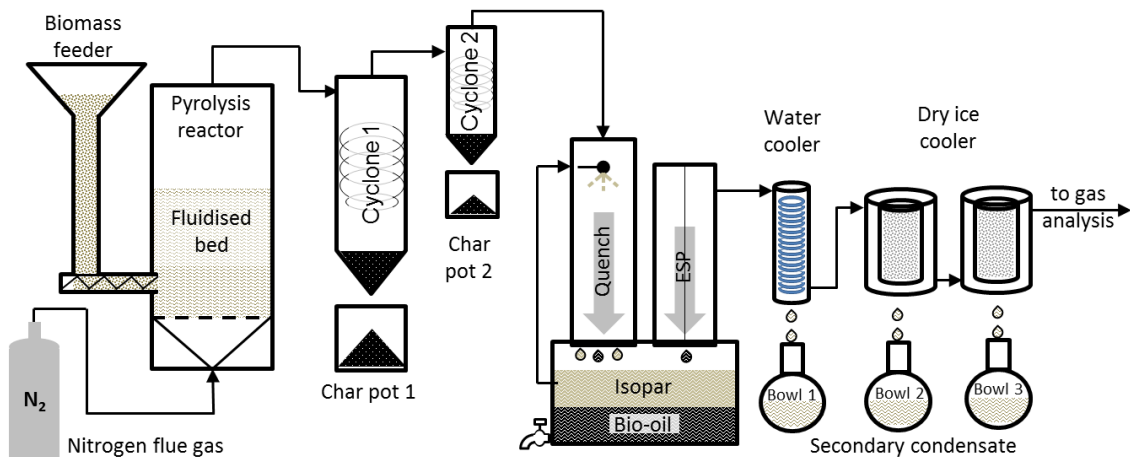
232 **Table 6.** Biochemical composition of the beech wood feedstock (%).

Water	Cellulose	Hemicellulose	Lignin	Ash	Others
12.95	40.26	21.68	19.91	1.62	3.58

233

234 The fast pyrolysis reactor is a fluidized bed reactor. The reactor bed consists of 1 kg quartz sand
 235 heated electrically and fluidized with pre-heated nitrogen. Two cyclones, a quench column and
 236 an electrostatic precipitator (ESP) separate and recover the pyrolysis products. As a quench
 237 liquid, a mixture of hydrocarbon isomers (ISOPAR) is used. Since the quench liquid is maintained
 238 at a temperature of 30 °C a significant amount of the process water is in the vapour phase, so
 239 an additional condensing system consisting of a water cooled condenser and two dry

240 ice/acetone condensers cool the vapours to around 0 °C. This condenses almost all the water
241 and light organics still contained in the gas stream and thereby yields a small amount of
242 secondary condensates, improving the mass balance closure significantly. The running time for
243 the verification experiments was 1.5 h for each run, processing about 1.5 kg of biomass
244 feedstock. The hot vapour residence time in the reactor was around 1.5 seconds. The char
245 recovered by the cyclones was collected, weighted and its elemental composition analysed. The
246 gas stream obtained after condensing the water was measured (based on the measured
247 volumetric flow) and analysed every three minutes by on-line gas chromatography (GC; Varian
248 micro gas chromatograph CP-4900). The condensed liquid, the bio-oil, was recovered and
249 separated from the quench liquid by decanting and centrifugation. The water content of the bio-
250 oil and the secondary condensate was then determined by Karl-Fischer titration. For analysing
251 the composition of the bio-oil, gas chromatography and mass spectroscopy (GC/MS; Varian 450
252 GC with FID and Varian 220 MS detector) was used. For this purpose, the bio-oil was dissolved
253 in ethanol and injected into the GC. In the same way, the secondary condensates obtained from
254 the dry ice/acetone condensers were analysed, as they contain a significant amount of light
255 organic substances.



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Figure 2. Setup of the experimental fast pyrolysis installation

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4.2. Simulation setup

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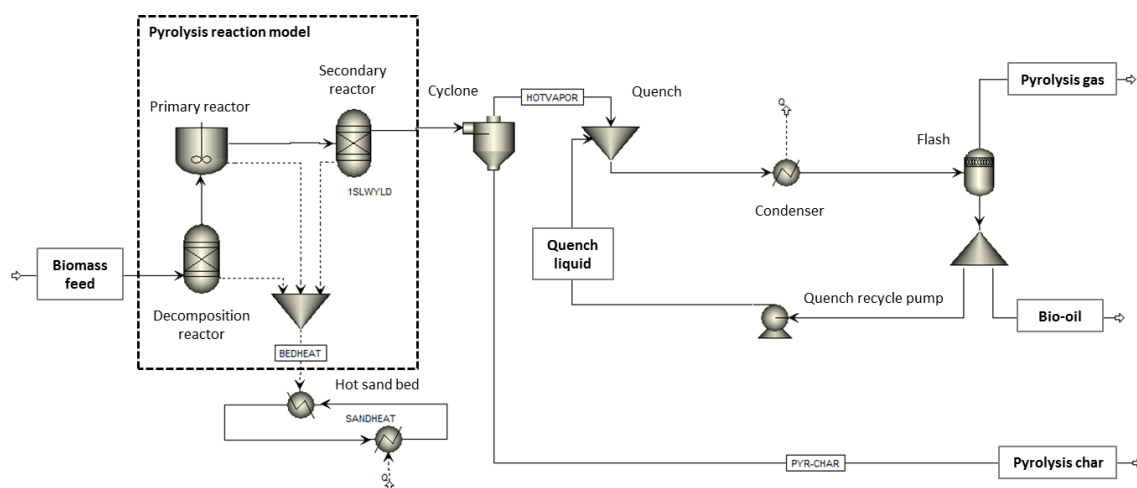
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In order to simulate the pyrolysis experiments, the same process parameters as in the experiments were used for the simulation. The gas residence time in the pyrolysis reactor was 1.5 seconds for all runs. Figure 3 shows a flowsheet of the simulation as used for reproducing the experimental runs. The pyrolysis reactor itself is represented by the three sub-reactors required for modelling the pyrolysis reactions as described previously. The simulation further uses one cyclone instead of the two in the experiments, and the gas-liquid separation is modelled by a flash at ambient pressure and ambient temperature. For this purpose, the condenser cools the quenched product stream down to 25 °C. Although the dry ice/acetone condensers in the experimental setup cool down the gas stream to temperatures around 0 °C, this is considered more realistic, since the condensate is obtained at ambient temperature.



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Figure 3. Flowsheet of the AspenPlus simulation setup as used for verification

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Furthermore, the lignin composition of the feedstock has to be determined as input for the reaction model. This is done by the iterative calculation procedure implemented in MS-Excel which adjusts the lignin composition to the given elemental and biochemical composition of the biomass. The lignin composition obtained in this way for the beech wood feedstock is presented in Table 7; details about the properties and elemental structure of the lignin fractions can be found in the SI.

Table 7. Lignin composition of the beech wood as used for the simulation

Lignin monomer	share
Lignin C	0.24%
Lignin O	31.88%
Lignin H	21.49%
LIG-M2	18.41%
LIG	0.35%
PLIG-C	0.44%
LIG-H	27.18%

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4.3. Verification results

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The results obtained from the experimental runs are compared with the simulation results in Tables 5 to 7. The analysis of bio-oil via gas chromatography (GC/MS) is generally difficult, and even with advanced methods and at the expense of considerable time only a few of the bio-oil compounds can actually be identified reliably [59]. Within the limited time available, only a CHN analysis of the bio-oil could be done, but with no detailed analysis of the bio-oil. Hence, only the elemental composition of the bio-oil is available for verification. The different runs are named with a number, denominating the reaction temperature in °C. The actual reactor bed temperature as measured by the thermocouples during the experiments is slightly higher than the target temperature, giving actual pyrolysis temperatures of 470, 520 and 570 °C.

294

295

The influence of reactor temperature on the pyrolysis products can be observed in Table 8, with the liquid yield achieving a maximum around 520°C. The yields of solids increase with lower

296 pyrolysis temperature due to incomplete pyrolysis, while it remains almost constant when
 297 increasing temperatures to 570°C. Mass closures of between 95.1% and 99.9% are achieved in
 298 the experimental runs. The simulation results agree very well with the experimental findings,
 299 with the highest correlation around 500°C and slightly increasing deviation for temperatures
 300 above and below. The temperature behaviour of the simulation in general is slightly less
 301 pronounced than in the experiments.

302 **Table 8.** Fraction yields (%) obtained in the experiments and from the simulation. The number
 303 denominates the reactor temperature of the run.

	470		520		570	
	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.
Gas	19.07	14.88	19.34	18.81	24.27	21.97
Oil	66.56	66.28	67.13	69.78	60.54	65.98
Char	14.27	18.82	10.62	11.39	10.31	12.03
Mass closure	99.89	99.99	97.10	99.99	95.12	99.99
Oil water cont	26.48	28.64	29.32	28.65	33.13	30.58

304
 305 The elemental composition obtained for the bio-oils from the experiments and the simulation
 306 runs are given in Table 6. When comparing the bio-oil composition with the elemental
 307 composition of the biomass, it can be seen that no fundamental changes occur; the hydrogen
 308 content increases and the carbon content decreases slightly, but no significant deoxygenation
 309 takes place. In general, the elemental composition of the bio-oil seems to be little affected by
 310 the reactor temperature; it is almost identical for the three beech wood runs. This is the case
 311 for both experiments and simulation, with the latter giving only slightly higher carbon and lower
 312 hydrogen content for the bio-oil (Table 9).

313
 314 **Table 9.** Bio-oil composition (% , ash free) obtained in the experiments and from the simulation.
 315 The number denominates the reactor temperature of the run.

Compound	470		520		570	
	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.
C	45.64	49.00	45.17	49.40	45.08	49.91
H	8.49	6.80	7.85	6.87	7.87	6.94
N	0.10	0.14	0.10	0.14	0.10	0.14
O	45.78	44.06	46.88	43.59	46.95	43.00

316
 317 Table 10 provides the detailed bio-oil composition broken down to basic bio-oil constituents as
 318 obtained from the simulation (detailed composition by functional groups). The quick
 319 degradation of the anhydrous sugar components, above all levoglucosan, can be observed with
 320 increasing temperature, while the degraded lignin fraction is independent of the pyrolysis
 321 temperature.

322
 323 **Table 10.** Detailed composition of the bio-oils (%) obtained from the simulation. The number
 324 denominates the reactor temperature of the run.

	470	520	550
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Water	28.64	28.65	30.58
Acids	6.80	6.11	6.24
Aldehydes	7.68	16.07	21.82
Ketones	1.66	3.44	4.73
PAH	0.00	0.04	0.07
Sugar derived	30.46	19.52	7.68
Furans	1.95	5.12	7.26
Alcohols	4.28	4.08	4.38
Lignin derived	17.86	16.32	16.57
Nitrogen	0.66	0.65	0.66

325

326 The elemental composition of the chars obtained is determined in the same way, with the
 327 corresponding results given in Table 11. Sulphur and chlorine content could not be determined
 328 by the available equipment and are not considered in the experimental runs. The char
 329 composition shows a maximum carbon content at 500°C, decreasing with lower and with higher
 330 temperatures. The simulation shows a more pronounced temperature behaviour and tends to
 331 give higher carbon yields and lower oxygen contents than the experiments for higher pyrolysis
 332 temperatures. However, overall the general temperature behaviour is reproduced fairly, and so
 333 also are the different results obtained for the two different feedstocks. For temperatures around
 334 500°C, results are very similar to the experiments, while again the discrepancies increase for
 335 higher and lower temperatures. The N content of the char is similar, but again the temperature
 336 behaviour is less pronounced.

337

338 **Table 11.** Char composition (%; ash free base) obtained in the experiments and from the
 339 simulation. The number denominates the reactor temperature of the run. -- = not measured

Compound	470		520		570	
	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.
C	79.58	72.46	85.04	93.63	80.02	91.45
H	3.60	3.06	3.81	1.26	3.05	2.25
O	16.57	24.11	10.79	4.63	16.82	5.92
N	0.25	0.28	0.37	0.32	0.11	0.23
S	--	0.09	--	0.16	--	0.15
Cl	--	0.00	--	0.00	--	0.00

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342 5. Discussion

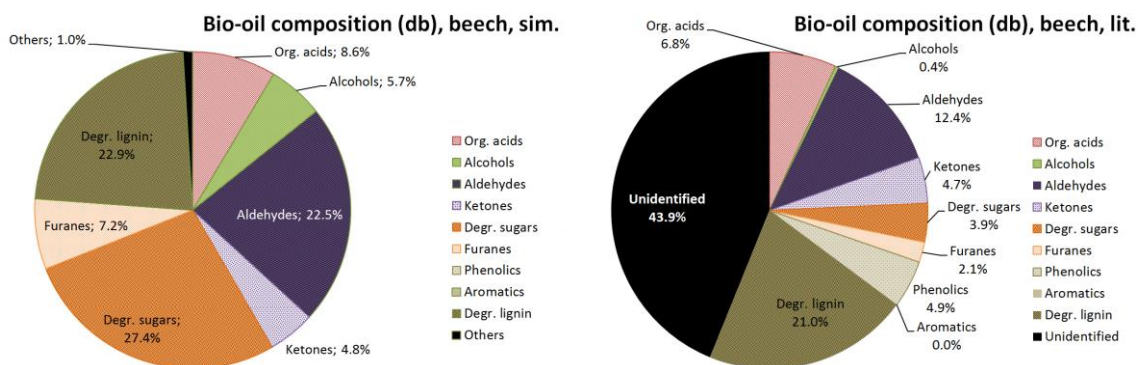
343 A good agreement can be observed between the experimental and the simulation results
 344 regarding fractional yields. The prediction of the yields is good and the temperature response
 345 also matches well. Highest agreement is found for typical pyrolysis temperatures of around
 346 500°C, with slightly increasing error towards higher and lower temperatures (Table 5). A similar
 347 result can be observed for the water content of the bio-oil, again with highest agreement for
 348 reaction temperatures of around 500°C. The simulation gives slightly lower water contents in
 349 comparison with the experiments, an effect that can also be observed when compared to
 350 existing literature data [38]. Furthermore, the increase in water content of the oil with increasing
 351 temperature is slightly more pronounced for the experimental findings; this indicates an

352 increasing error in the prediction of the water content at temperatures above or below the
353 typical pyrolysis temperature of 520 °C. Still, the agreement between experiments and
354 simulation in general is high.

355 Regarding the product compositions, a good correlation can be found for the atomic
356 composition of the chars and for the bio-oils, with the best matching results at around 500°C.
357 The simulation further tends to give a higher content of nitrogen containing species in the bio-
358 oil. However, a good match is obtained for the N fraction of the char, except for higher pyrolysis
359 temperatures, where the strong decrease of N observed in the experiments is not reproduced
360 by the simulation. The content of S and Cl of the char was not analysed in the experiments and
361 can therefore not be compared.

362 A detailed analysis of the fractional composition of the bio-oil from the experiments could not
363 be achieved. The results that were obtained by conventional GC/MS analysis of the bio-oil were
364 found to be unsuitable for verification since the results are fundamentally different to the typical
365 values published widely in the literature [6,60–63]. This is in-line with the findings published by
366 Brodzinski in her dissertation [59], who analysed bio-oil and found the light aldehyde and volatile
367 acid content of the bio-oil to be undetectable via conventional GC/MS, since the solvent peaks
368 cover the peaks of these volatile compounds. Nevertheless, a qualitative validation can be done
369 with the data published by Brodzinski, who gives an exhaustive analysis of a bio-oil obtained
370 from beech wood. Figure 4 gives a comparison of the bio-oil composition obtained in her work
371 for beech wood (8.9% moisture) with the one obtained from the simulation. Comparison is done
372 on a dry base, since the beech wood used by Brodzinski had a lower water content. Good
373 agreement is found for the proportion of degraded lignins, organic acids and ketones, while for
374 the alcohol, aldehyde and especially, the degraded sugar fraction significantly higher
375 proportions are obtained. On the other hand, almost 44% of the bio-oil remains unidentified by
376 Brodzinski, and hence must be part of one of the fractions.

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380 **Figure 4.** Comparison of the composition of beech wood bio-oil obtained from simulation (left)
381 and from literature [59] (right); dry base

382

383 6. Conclusions

384 The kinetic reaction model presented in this paper as implemented in Aspen Plus predicts the
385 pyrolysis reactions for lignocellulosic biomass as a function of the biomass composition and
386 reactor conditions. It shows the typical yield curves for pyrolysis reactions and with good
387 agreement with existing literature data on pyrolysis yields and product composition. Maximum
388 bio-oil yield is predicted for temperatures around 500°C, and oil yields are notably higher for a

389 woody feedstock like pine wood than for straw. Only for higher temperatures above the range
390 of typical pyrolysis conditions, an increasing error can be observed, which limits the applicability
391 of the model for extreme conditions. The experimental validation in a $1 \text{ kg}\cdot\text{h}^{-1}$ continuous
392 fluidised bed reactor in the installations of the Bioenergy Research Group (BERG) of Aston
393 University further underlines these findings. A high agreement regarding fraction yields and
394 water content of the bio-oil can be observed, and also for the elemental composition of the bio-
395 oil and the char product. While a detailed determination of the fractional composition of the
396 bio-oil obtained from the experiments was not possible, a comparison with published work on
397 the composition of bio-oil from beech wood produced under similar conditions shows good
398 agreement. The reaction model can therefore be considered a valuable tool for calculating the
399 yields and the composition of the products for pyrolysis of lignocellulosic biomass.

400 Up to now, process analysis of pyrolysis processes used simple models based on black box
401 approaches and with a strongly simplified composition of the bio-oil. This is the first work that
402 presents a comprehensive kinetic reaction model that can be readily implemented in AspenPlus
403 and similar process simulation software packages. The predictive approach and the detailed
404 modelling of the bio-oil allows a better estimation of the properties of bio-oils obtained from
405 different types of lignocellulosic biomass under different pyrolysis conditions (including fast and
406 slow pyrolysis) without the need for case-specific pyrolysis experiments. As such, it will permit
407 quicker and more reliable system analysis of all kind of pyrolysis processes. The detailed
408 information about stream compositions that can be obtained from the model also eases the
409 analysis and optimisation of pyrolysis processes on a plant level, allowing more precise
410 thermodynamic and economic assessments, but also the estimation of potential environmental
411 impacts of such processes.

412

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602

603 **Abbreviations**

604	ESP	Electrostatic precipitator
605	GC	Gas chromatography
606	MS	Mass spectroscopy
607	RYield	Aspen Plus reactor type: Black box type reactor where the yields of the
608		reaction products are specified for a given feed
609	RGibbs	Aspen Plus reactor type: Calculates the reaction products by Gibbs free
610		energy minimization (thermodynamic equilibrium)
611	RCSTIR	Aspen Plus reactor type: Kinetic reactor for simulating reactors with
612		perfect mixing of the reactants; requires specification of the reaction
613		kinetics
614	RBatch	Aspen Plus reactor type: Kinetic reactor for simulating batch type
615		reactors; allows for defining temperature profiles. Requires specification
616		of the reaction kinetics
617	ULTANAL	Ultimate analysis – atomic composition (C, H, N, O, S, Cl)
618	PROXANAL	Proximate analysis – fractional composition (volatile matter, fixed
619		carbon, water content)
620	PAH	Polycyclic aromatic hydrocarbon
621	ar	As received
622	db	Dry base

623